CHARACTERIZATION OF ANISOTROPIC PARTICLES BY RHEO-OPTICS

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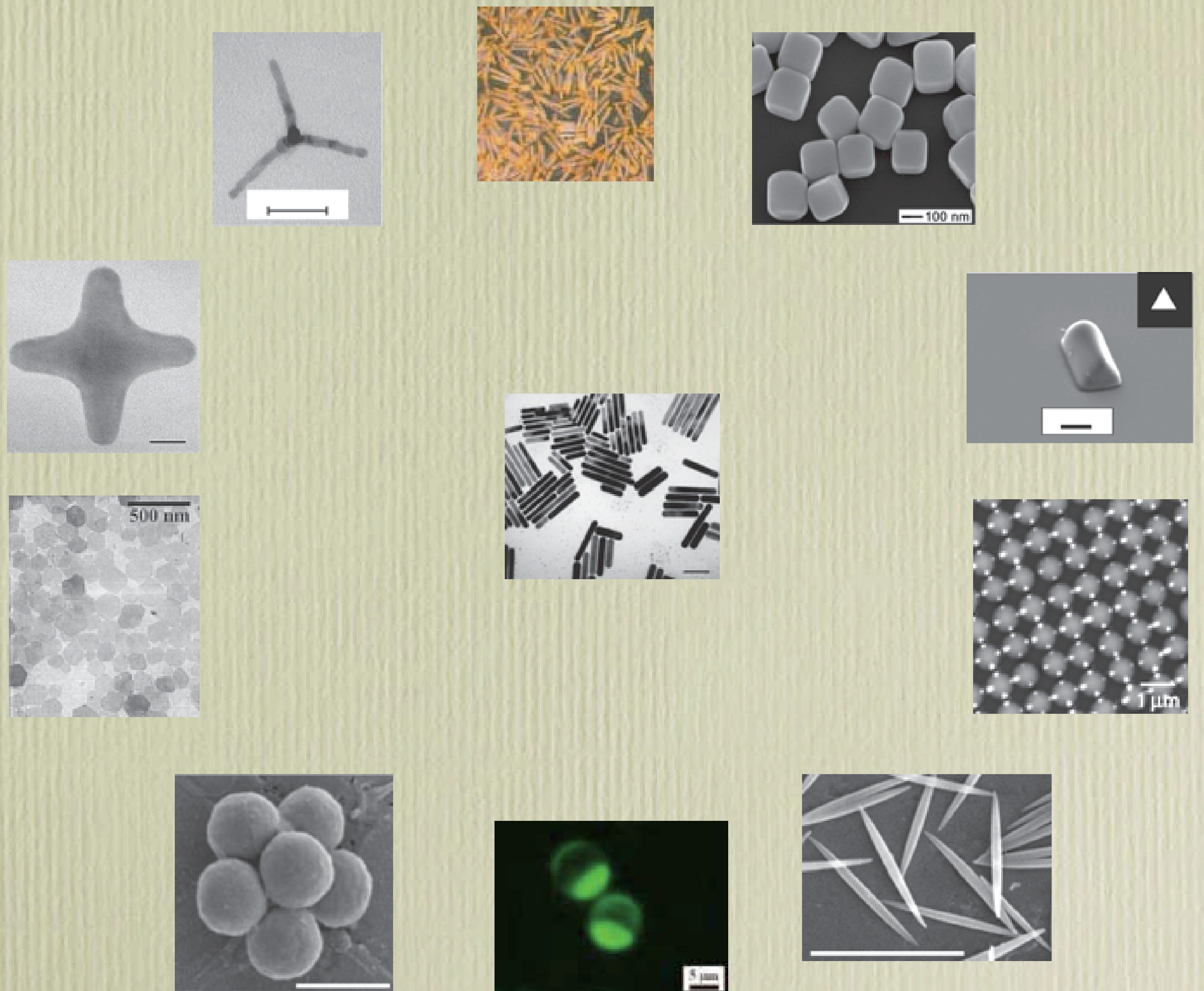
Anisotropic Nano-Particles

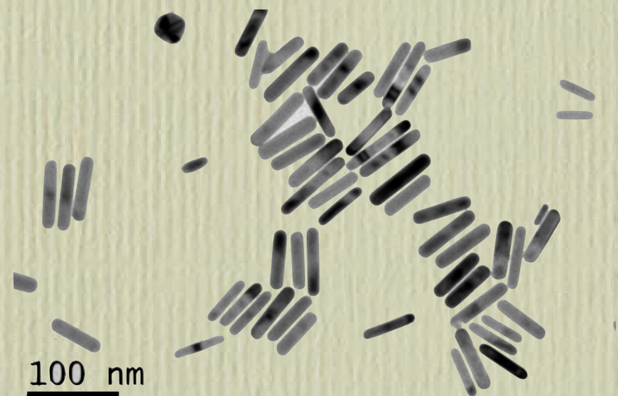


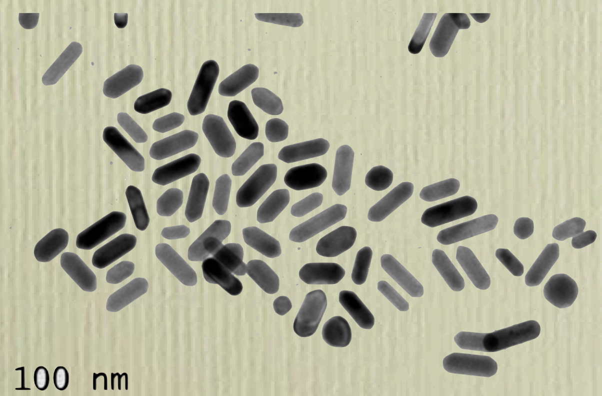
S. C. Glotzer and M. J. Solomon Nature Materials, **6** 2007 557

Introduction

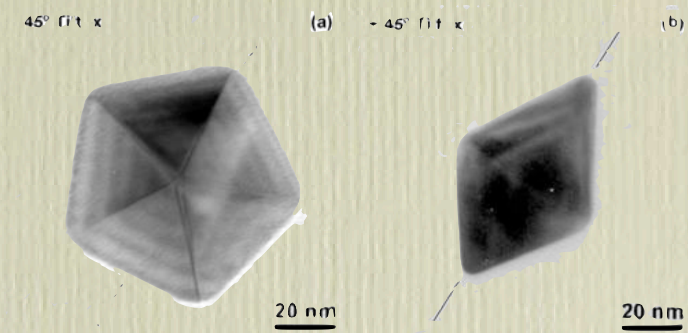
Anisotropic nano-particles

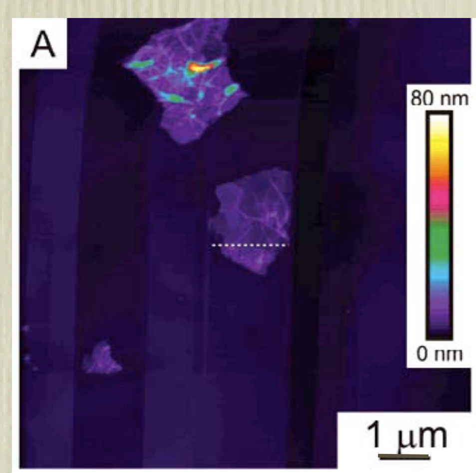
Rods





Disks





Characterization Methods

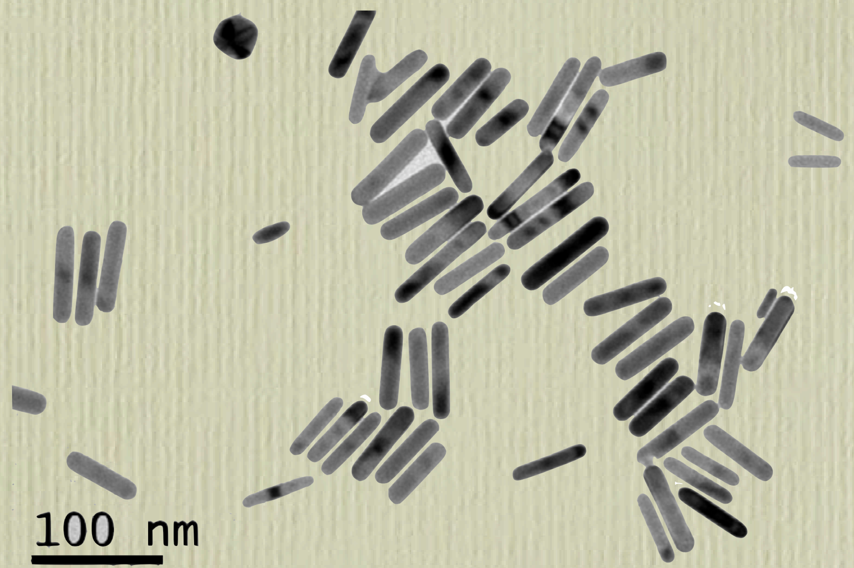
1. Transmission Electron Microscopy (TEM)
   Image analysis

2. Dynamic Light Scattering (DLS)
   Diffusion

3. Rheo-optics
   Tumbling

TEM

Image analysis



Calibration using **scale bar**

Particle dimensions **L** and **W** are obtained for **100-150 particles**

Sample	L (nm)	W (nm)	AR_{TEM}
GoldRod-1	56.29 ± 5.83	20.86 ± 2.94	2.76 ± 0.52
GoldRod-2	61.66 ± 7.18	18.16 ± 0.47	3.43 ± 0.47
GoldRod-3	66.69 ± 6.14	15.61 ± 1.93	4.33 ± 0.65

DLS

Dynamic light scattering is based on diffusion

Two parts

1. Translational diffusion
2. Rotational diffusion

Diffusion of rod like particles

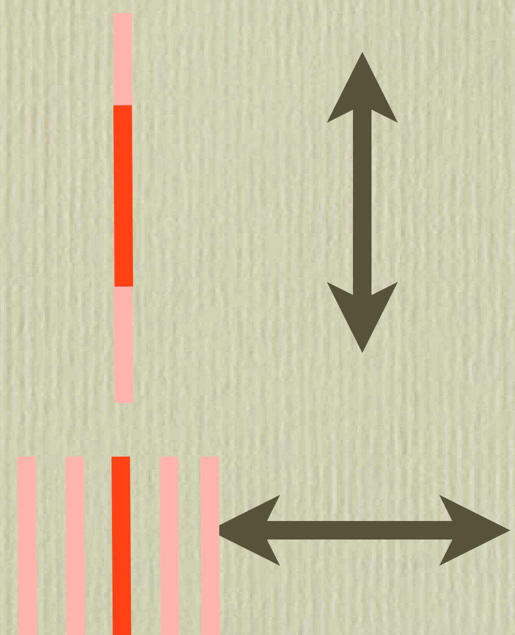
Courtesy: Pavlik Lettinga

DLS

Translational Diffusion $(\bar{D})$

D_{II}

$D_{\perp}$



$$\bar{D}_{avg} = \frac{2D_{II} + D_{\perp}}{3}$$

Translational diffusion

Courtesy: Pavlik Lettinga

DLS

Rotational Diffusion (D_r)

D_r

$D_{spin} \equiv$ fast (cannot be detected)

$$D_r = D_r$$

Rotational+Translational diffusion

Courtesy: Pavlik Lettinga

DLS

Diffusion data analysis

$$I(Q,\omega) = I_{iso}(Q,\omega) + I_{aniso}(Q,\omega) \qquad I(Q,\omega) \propto S(Q,\omega)$$

Auto correlation function

$$g_1(t) = \tilde{S}_{iso}(Q,t) + \tilde{S}_{aniso}(Q,t)$$

Decomposition into VV and VH gives

$$g_1^{VV}(Q,t) = A exp\{-\bar{D}Q^2 t\} + B\exp\{-(\bar{D}Q^2 + 6D_r)t\}$$

$$g_1^{VH}(Q,t) = \exp\{-(\bar{D}Q^2 + 6D_r)t\}$$

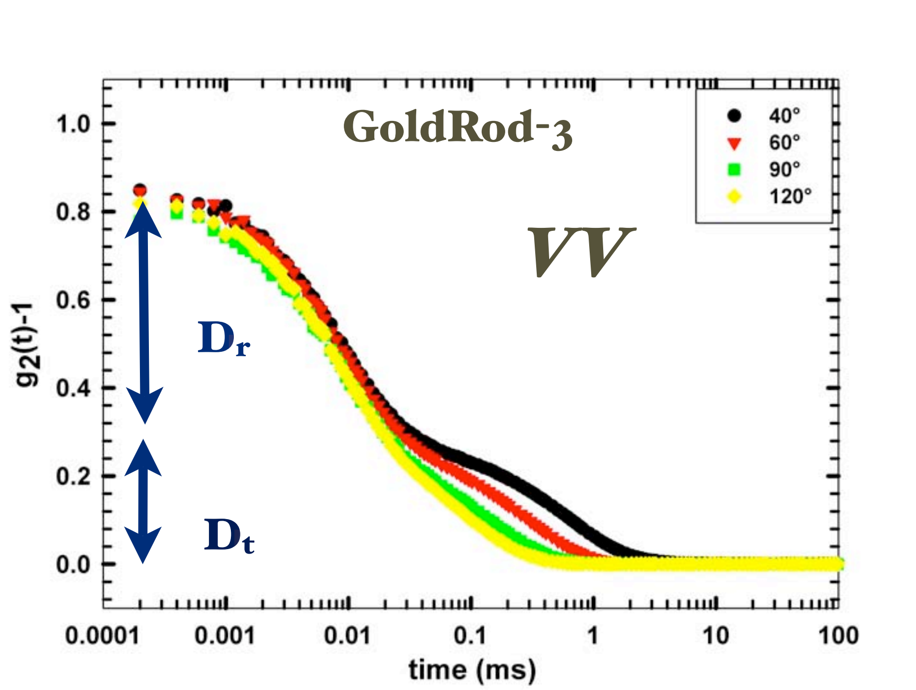
$$g_2(Q,t) = 1 + \beta[g_1(Q,t)]^2$$

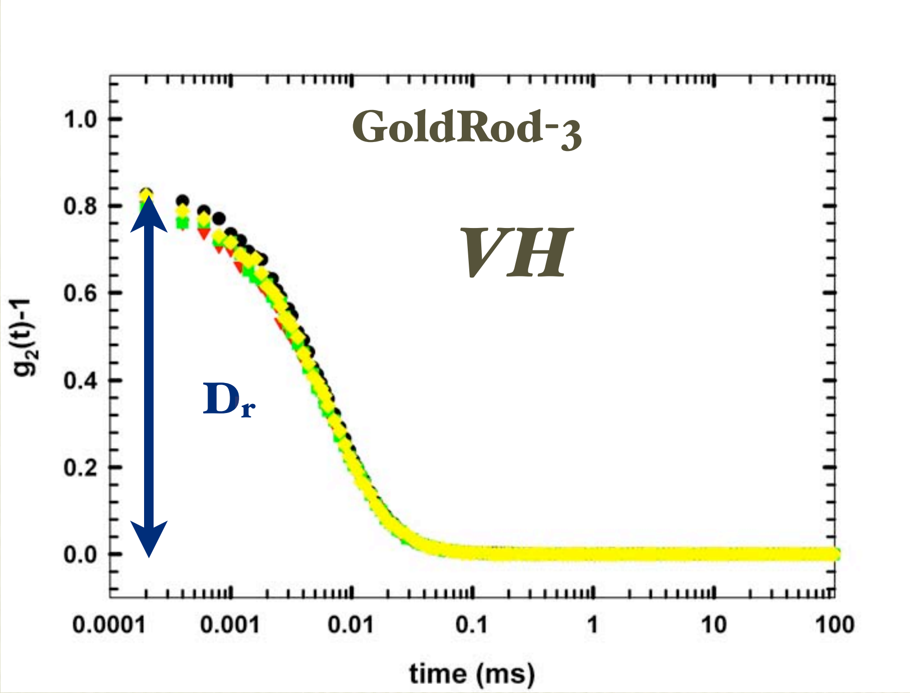
Pecora, R. *J. Chem. Phys.* **1968**, 49, 1036

Jessica, R. et al., *J. Phys. Chem. C* **2007**, 111, 5020

DLS

Results from DLS





Translational + Rotational

$$g_2^{VV}(Q,t)-1=\beta[A^2 exp\{-\Gamma t\}+$$
$$2AB\exp\{-(\Gamma+\Delta/2)t\}+B^2\exp\{-(\Gamma+\Delta)t\}]$$

$$\Gamma=2\bar{D}Q^2 \qquad \Delta=12D_r$$

Rotational

$$g_2^{VH}(Q,t)-1=\beta'\exp\{-(\Gamma+\Delta)t\}]$$

$$A+B=1$$

Jessica, R. et al., *J. Phys. Chem. C* **2007**, 111, 5020

DLS-aspect ratio

Method 1

$$\bar{D} = \frac{k_B T(\ln(L/d_{cs}) + \bar{C})}{3\pi\eta L}$$

$$\bar{C} = 0.312 + 0.565\frac{d_{cs}}{L} - 0.100\left(\frac{d_{cs}}{L}\right)^2$$

$$D_r = \frac{3k_B T(\ln(L/d_{cs}) + C_r)}{\pi\eta L^3}$$

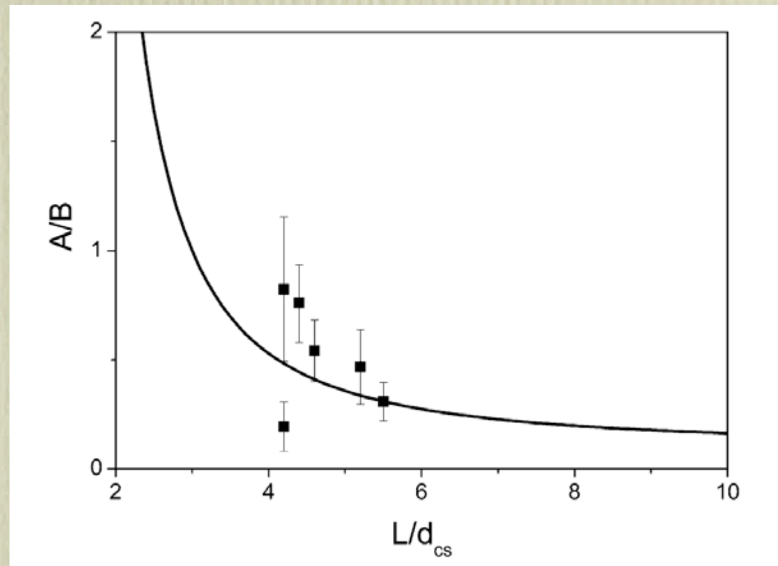
$$C_r = -0.662 + 0.917\frac{d_{cs}}{L} + 0.05\left(\frac{d_{cs}}{L}\right)^2$$

$$L^3 = \frac{3k_B T}{4\eta_o D_r}$$

d_{cs} should be adjusted

Method 2

$$\frac{A}{B} = \frac{5}{4}\frac{\alpha_{11}{}^2}{\langle(\alpha_\perp - \alpha_{11})^2\rangle}$$



Broersma S. *J. Chem. Phys.* **1960**, 32, 1626,1632
Ortega A. Garcia de la Torre *J. Chem. Phys.* **2003**, 119, 9914
Pecora, R. *J. Chem. Phys.* **1968**, 49, 1036
Jessica, R. et al., *J. Phys. Chem. C* **2007**, 111, 5020

DLS

Results from DLS

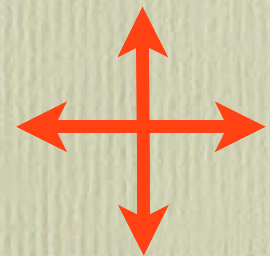
Sample	D_t (nm^2/ms)	D_r (ms^{-1})	AR Method 1	D_t (nm^2/ms)	D_r (ms^{-1})	AR Method 2
GoldRod-1	1,09E+04	15,79	2,22	1,02E+04	8,89	2,58
GoldRod-2	9,67E+03	15,24	2,66	1,00E+04	8,58	3,19
GoldRod-3	9,64E+03	14,09	3,16	1,06E+04	8,1	3,43

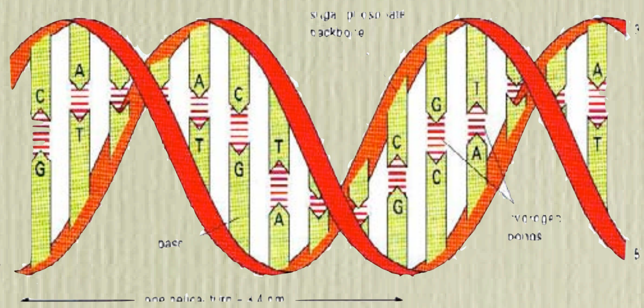
Sample	AR_{TEM}
GoldRod-1	2.76 ± 0.52
GoldRod-2	3.43 ± 0.47
GoldRod-3	4.33 ± 0.65

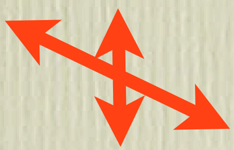
Rheo-optics

Basics

Scattering and/or adsorption of light depends on the polarization state







Linearly polarized light in x and y direction

Change in polarization angle and amplitude

Rheo-optics

Dichroism

"the difference between the imaginary parts of the refractive indices of the medium measured parallel an perpendicular to the average particle orientation"

$$\Delta n'' = n''_{11} - n''_{\perp}$$

$$DC_{signal} = \frac{I_o}{2}\cosh(\delta'')$$

$$I_\omega = -2J_1(A)\frac{I_o}{2}\sin(2\theta)\sinh(\delta'')$$

$$I_{2\omega} = -2J_2(A)\frac{I_o}{2}\cos(2\theta)\sinh(\delta'')$$

$$R_1 = \frac{I_\omega}{\left(I_o/2\right)\cosh(\delta'')} = -2J_1(A)\sin(2\theta)\tanh(\delta'')$$

$$R_2 = \frac{I_{2\omega}}{\left(I_o/2\right)\cosh(\delta'')} = -2J_2(A)\cos(2\theta)\tanh(\delta'')$$

Fuller, G. G., *Optical Rheometry of Complex Fluids*, Oxford Univ. Press Oxford (1995)

Rheo-optics

Dichroism ....

$$\theta = \frac{1}{2}\tan^{-1}\left[\frac{R_1/J_1(A)}{R_2/J_2(A)}\right]$$

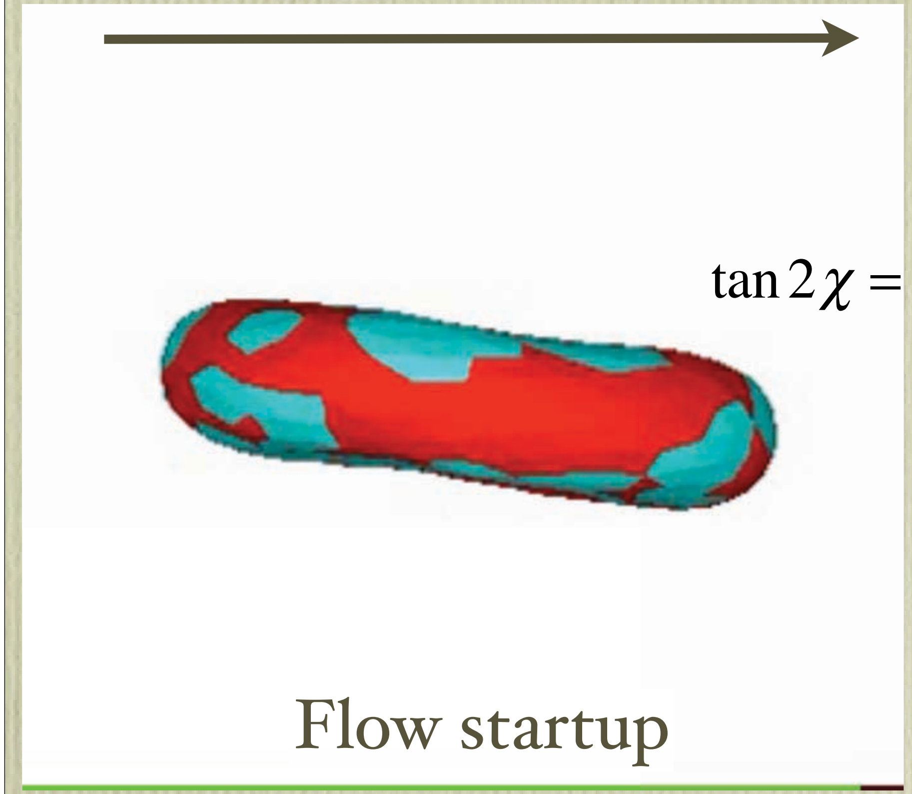
$$\delta'' = (sign(R_2))\tanh^{-1}\left(\frac{1}{2}\sqrt{\left(R_1/-J_1(A)\right)^2 + \left(R_2/-J_2(A)\right)^2}\right)$$

$$\Delta n'' = \frac{\delta''\lambda}{2\pi d}$$

Fuller, G. G., *Optical Rheometry of Complex Fluids*, Oxford Univ. Press Oxford (1995)

Rheo-optics

Tumbling



$$\tan 2\chi = \frac{2\int_0^\infty (r - r^{-1})\sin\left(\frac{4\pi t}{T}\right) g(r)dr}{\int_0^\infty \left[(r^2 - r^{-2}) - (r^2 - r^{-2})\cos\left(\frac{4\pi t}{T}\right)\right] g(r)dr}$$

Tumbling of red blood cell in shear flow

$$T = \frac{2\pi}{\dot{\gamma}}(r + \frac{1}{r})$$

$$g(r) = \frac{1}{\sqrt{2\pi\sigma}}\exp\left(-\frac{(r-\bar{r})^2}{2\sigma^2}\right)$$

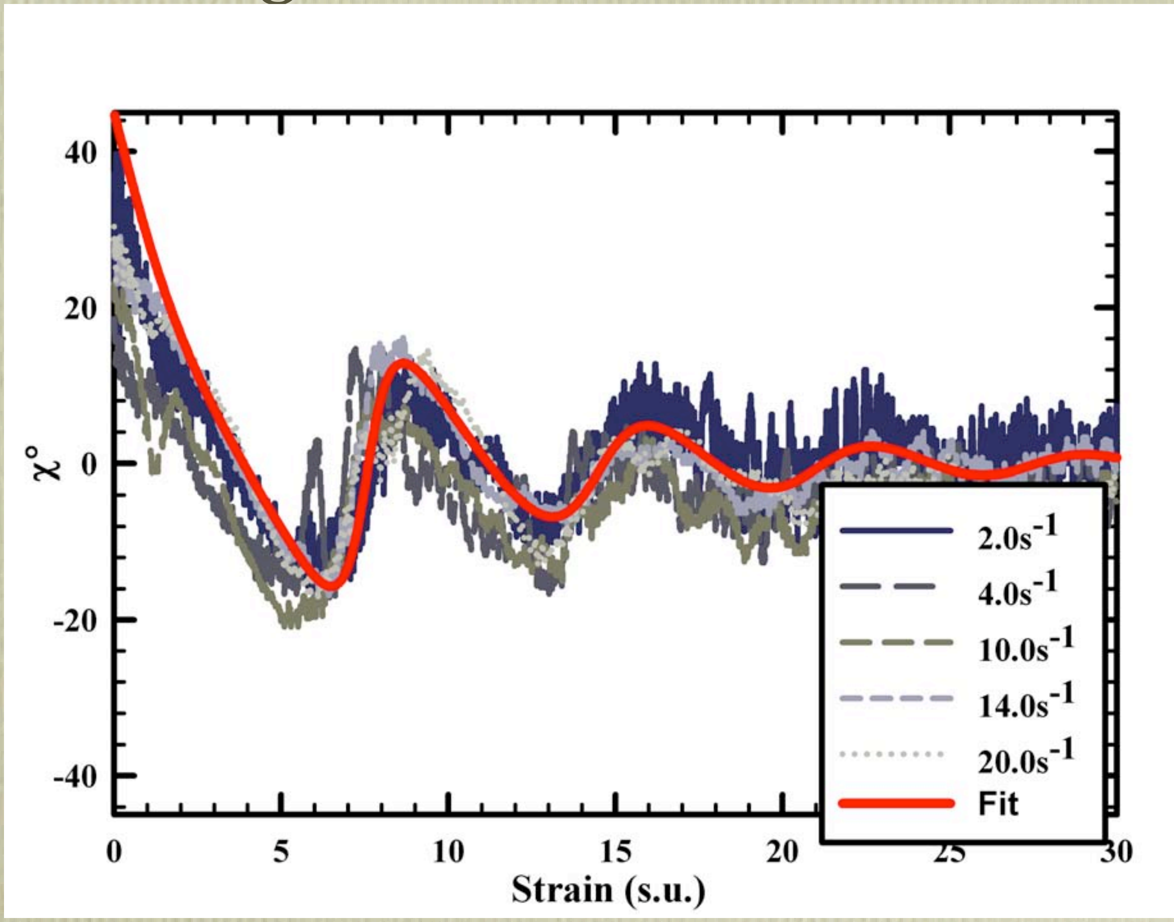
Vermant, J. et al., *AIChE.* **2001**, 47, 790

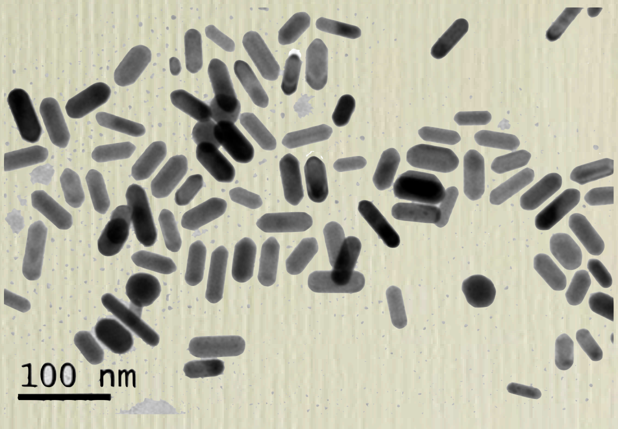
Movie from NIBIB

Rheo-optics

Tumbling

Gold rods 1



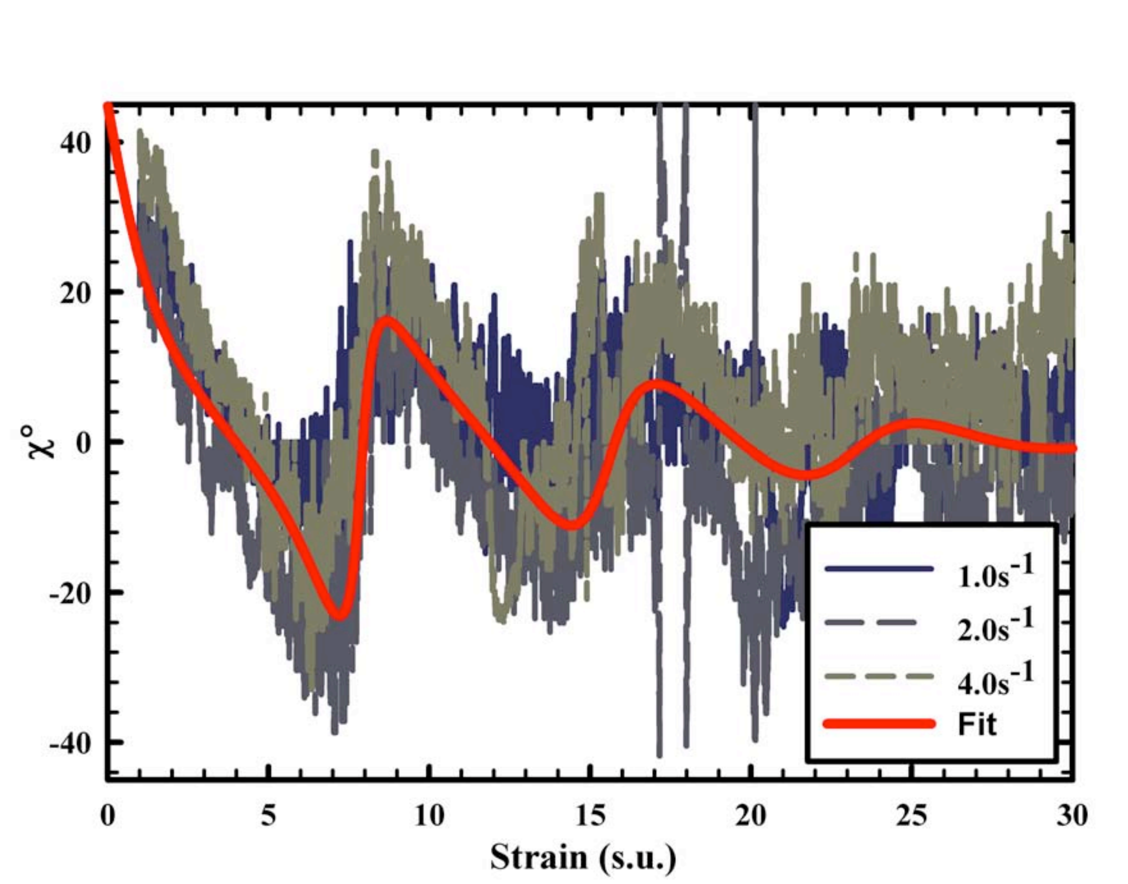


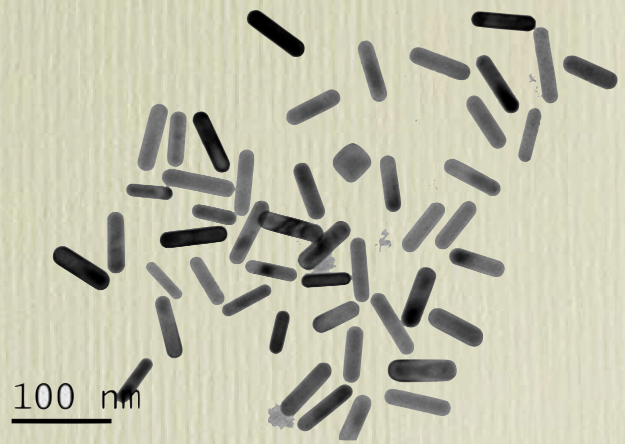
	AR	polydisp
GoldRod-1	1,7	0,6

Rheo-optics

Tumbling

Gold rods 2

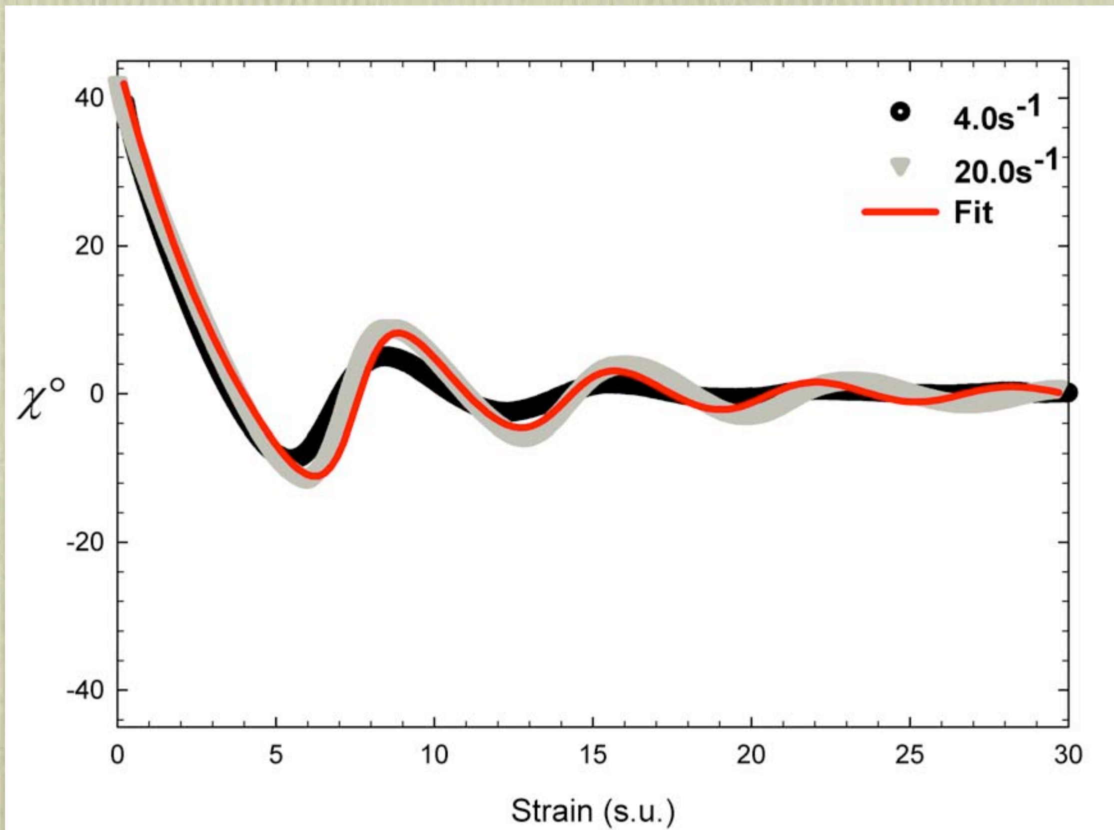




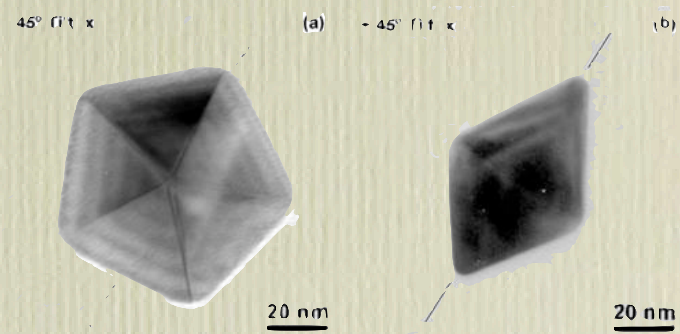
	AR	polydisp
GoldRod-2	2,0	0,6

Rheo-optics

Tumbling



Gold disks



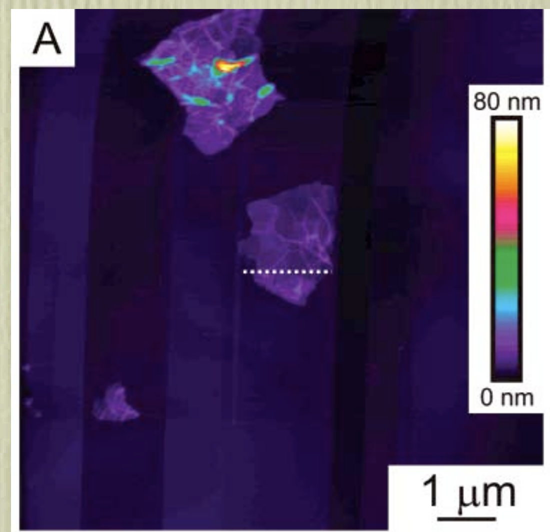
	AR	polydisp
GoldDisks	0,556	0,7

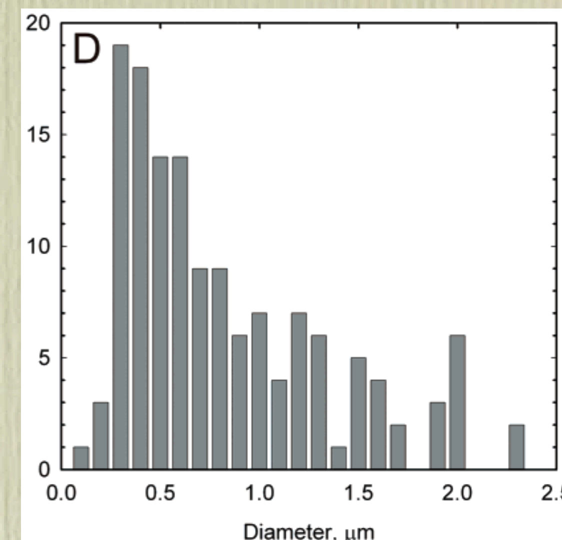
Comparison of Results

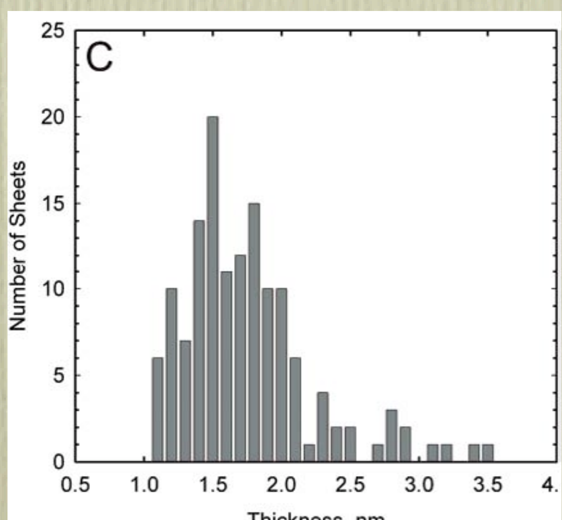
	TEM	DLS	Dichroism	
Sample	AR	AR	AR	polydisp.
GoldRod-1	2,76	2,58	1,7	0,6
GoldRod-2	3,43	3,19	2,0	0,6
GoldRod-3	4,33	3,43	-	-
GoldDisk	0,5	-	0,556	0,7

Rheo-optics

Graphene







Mean thickness *1.7 nm*

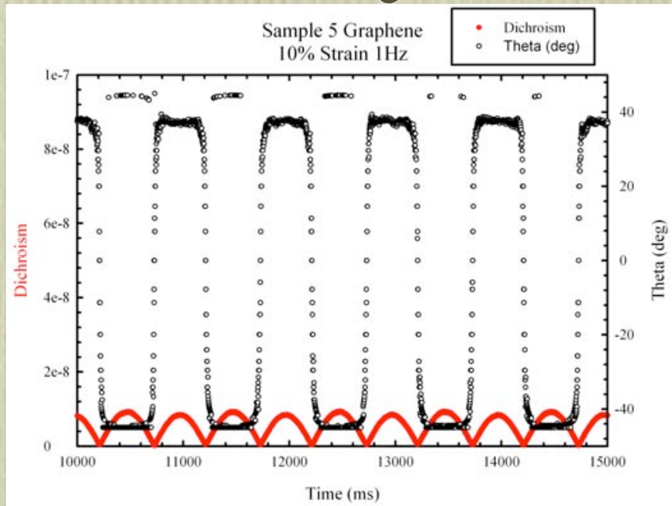
Surface area

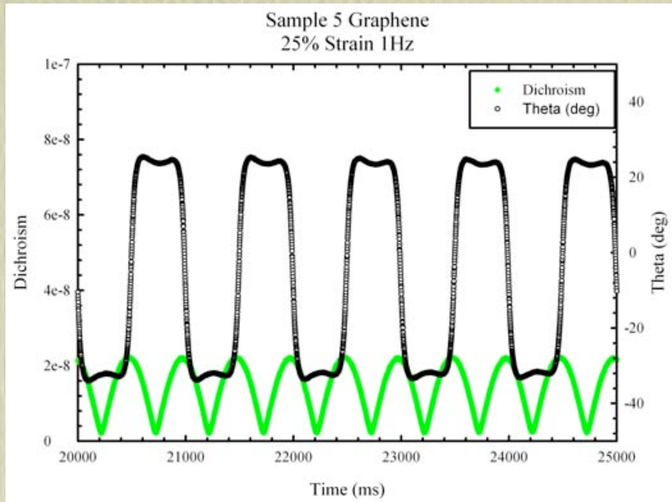
600-900 m^2/g (BETNitrogen)

1850 m^2/g (MB dye Ethanol Suspension)

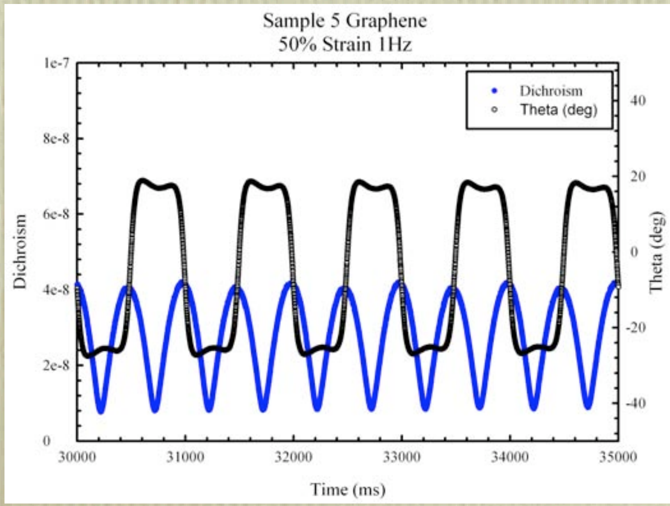
Rheo-optics

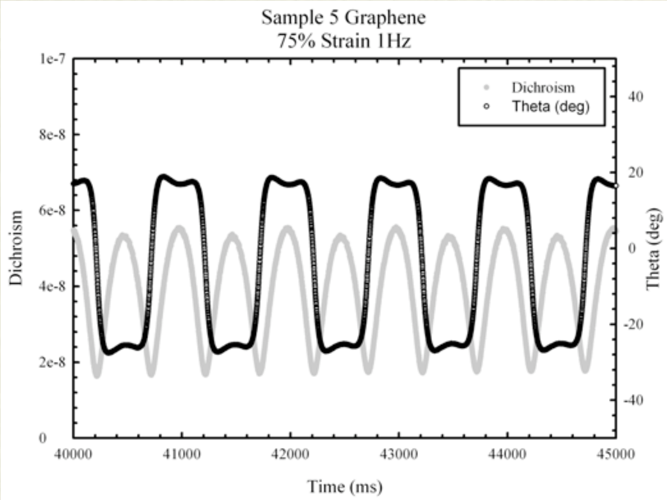
Oscillatory





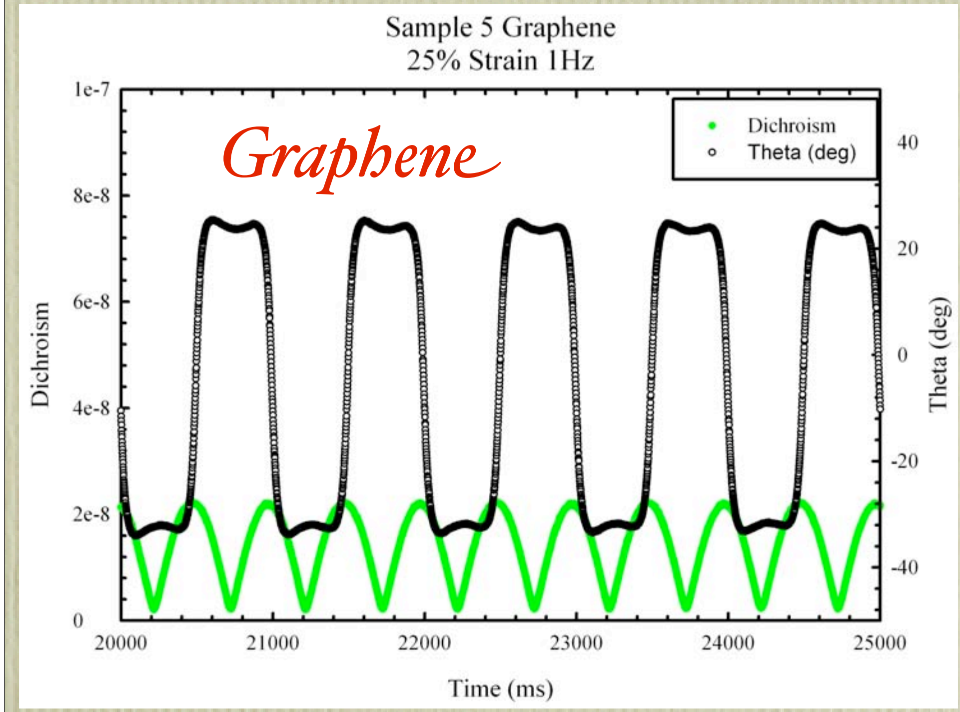
1 Hz

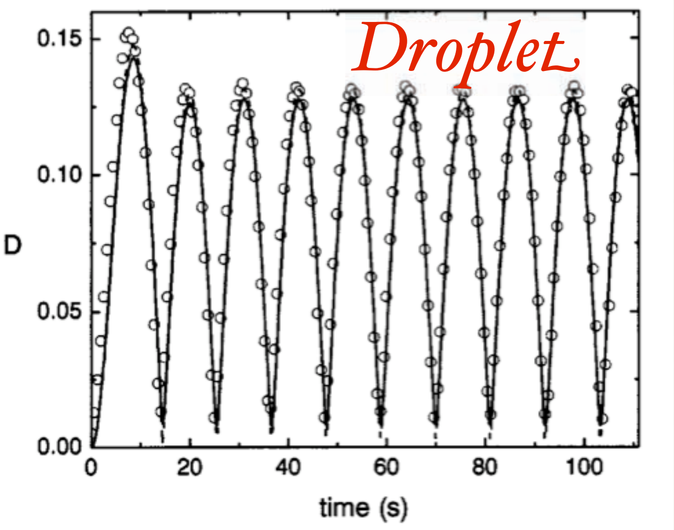


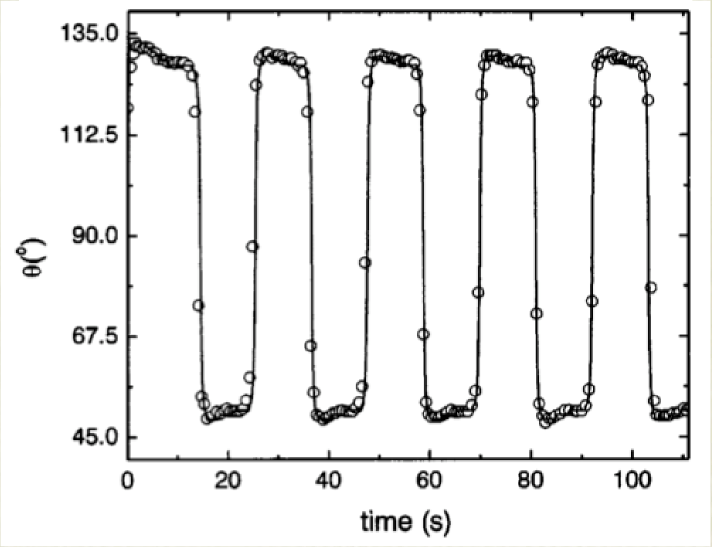


Rheo-optics

Comparison with droplets







Conclusions

Characterization methods for anisotropic nanoparticles

-TEM - physical aspect ratio (less statistics)

-DLS give a good approximation of hydrodynamic aspect ratio

. Assumption - stabilizing layer thickness (method-1)

. Method-2 can be used only for 2>AR<20

. No information about polydispersity

-Rheo-optics - hydrodynamic aspect ratio and polydispersity

. Assumption - ellipsoid - small aspect ratio

. Pe number should be high

. Can be extended to sheets (platelets)

Thank You

Comparison of Diffusion in Water and Gly

	Water		Glycerol	
Sample	D_t (nm^2/ms)	D_r (ms^{-1})	D_t (nm^2/ms)	D_r (ms^{-1})
GoldRod-1	1,09E+04	15,79	4,9	8,60E-03
GoldRod-2	9,67E+03	15,24	5,06	6,87E-03
GoldRod-3	9,64E+03	14,09	7,2	8,40E-03

Viscosity ratio (G/W)=1,5e-3

Glycerol to water conversion		
Sample	D_t (nm^2/ms)	D_r (ms^{-1})
GoldRod-1	7,70E-03	13,52
GoldRod-2	8,00E+03	10,8
GoldRod-3	1,08E+04	12,6

Thin and thick particles

$$I \propto V^2 \propto D^4 L^2$$

25% reduction in diameter
will cause
70% reduction in scattered intensity

Gold disk has better averaging than GoldRod-3

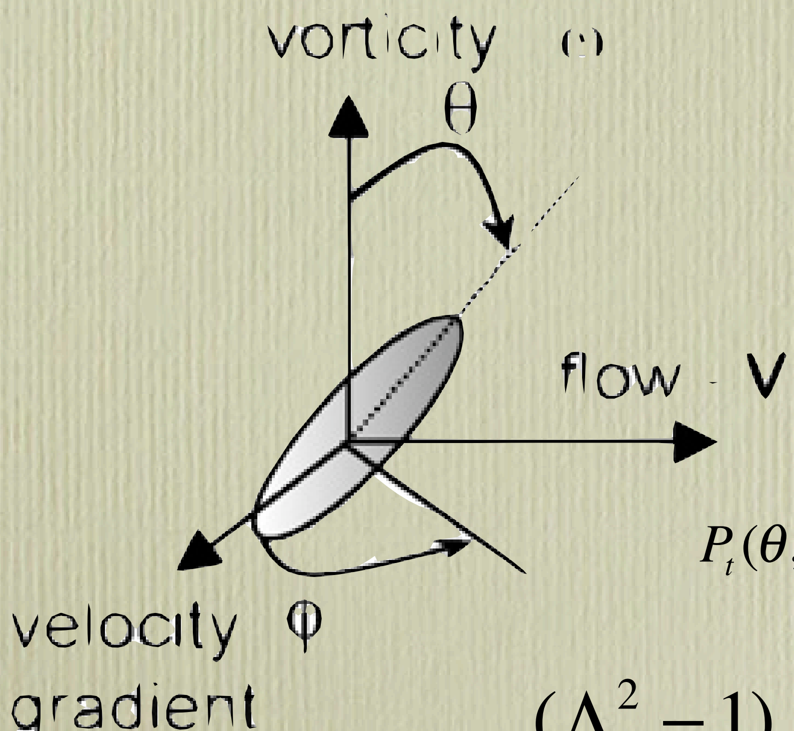
Dichroism derivation

Results for ellipsoid tumbling by Jeffrey

$$\tan\theta = \frac{C\cdot r}{\sqrt{\left(r2\cos 2\phi + \sin 2\phi\right)}}$$

$$\phi = \tan^{-1}\left(r\cdot\tan\left(\frac{2\pi t}{T} + \kappa\right)\right)$$

$$T = \frac{2\pi}{\dot{\gamma}}\left(r + \frac{1}{r}\right)$$



$$\tan(2\chi) = \frac{\left\langle \sin^2\theta\sin 2\phi\right\rangle}{\left\langle \sin^2\theta\cos 2\phi\right\rangle}$$

$$\langle\ldots\ldots\rangle = \int_0^{\pi}\int_0^{2\pi} \ldots P_{t,\sigma}(\theta,\phi,\bar{r})\,d\phi\, d\theta$$

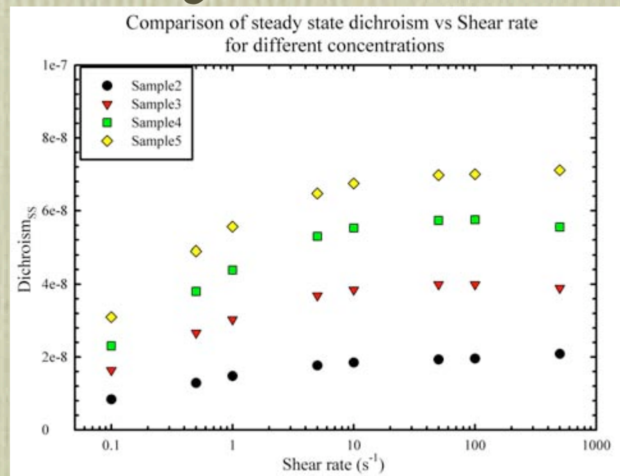
$$P_t(\theta,\phi,r) = \frac{\sin\theta}{4\pi}\left[1 - \frac{3}{2}(\Lambda^2 - 1)\sin 2\theta\right] + \Theta\left[(\Lambda^2-1)\right]$$

$(\Lambda^2 - 1)$ is small for particles close to sphere

Small polydispersity

Rheo-optics

Steady state



$$T = \frac{2\pi}{\dot{\gamma}}(r + r^{-1})$$

T = period of oscillation
r = aspect ratio
ɣ = Shear rate

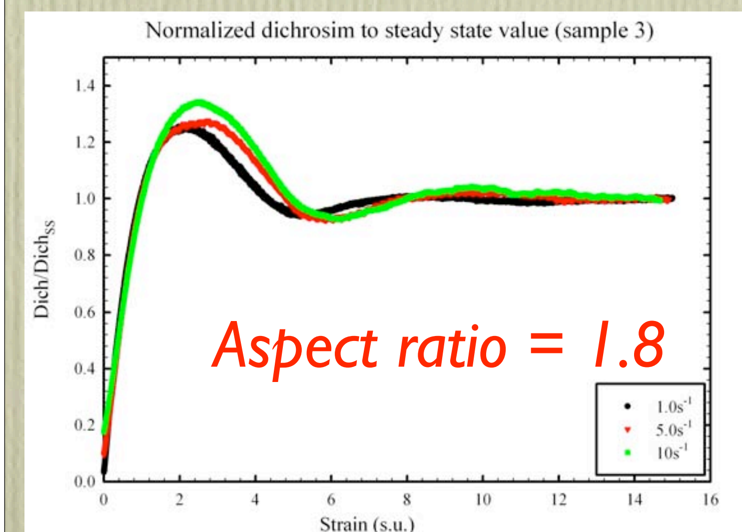
d = 345 nm

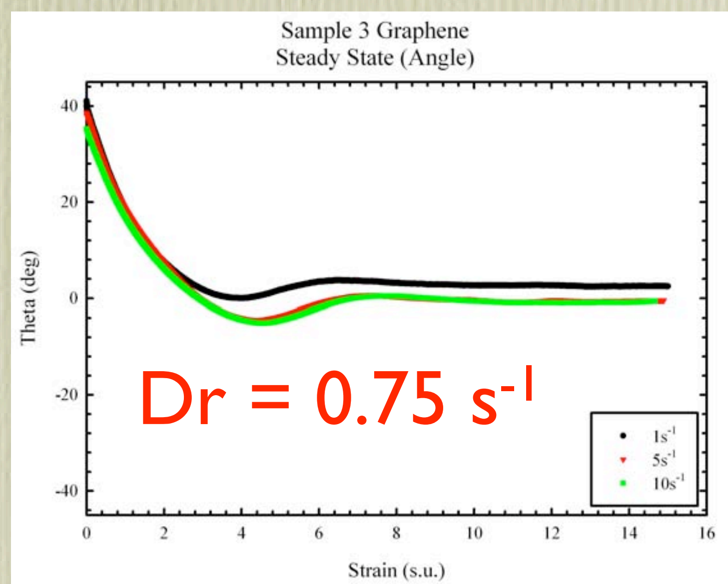
$$d^3 = \frac{3k_B T}{4\eta_o D_r}$$

$6D_r^{-1} = b$

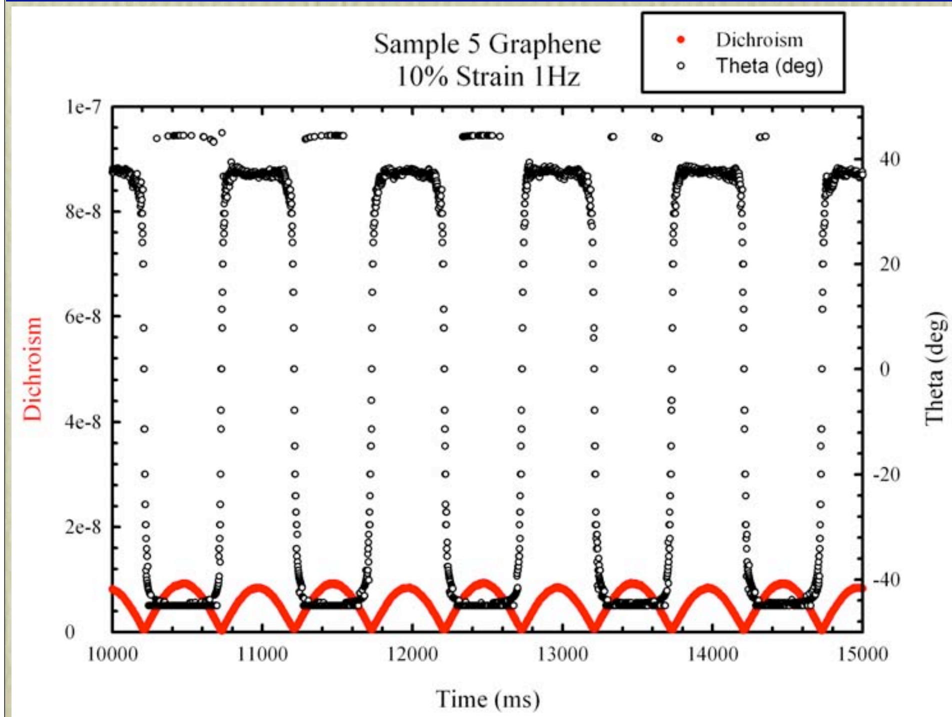
exp. decay from relaxation

d = diameter

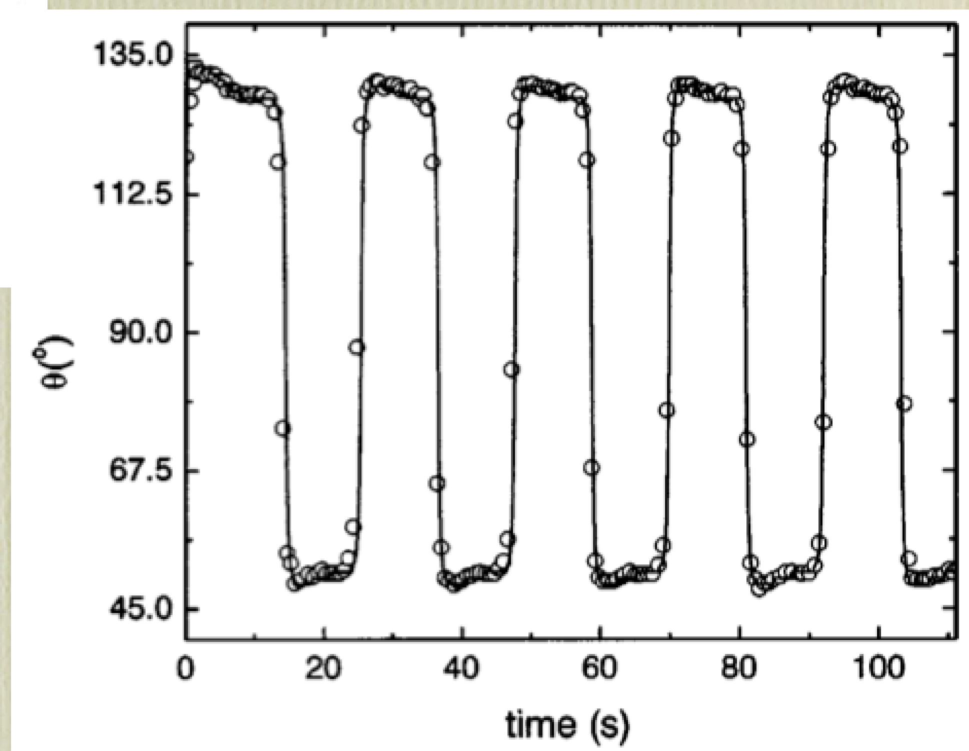




extra



Sample 5 Graphene
10% Strain 1Hz
Dichroism
Theta (deg)
1e-7
8e-8
6e-8
4e-8
2e-8
0
40
20
0
-20
-40
10000
11000
12000
13000
14000
15000
Time (ms)
Dichroism
Theta (deg)



135.0
112.5
90.0
67.5
45.0
θ(°)
0
20
40
60
80
100
time (s)